

# Ethylene/Propylene Copolymerization Using $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$ Catalyst: Effects of Copolymerization Conditions on Viscosity Average Molecular Weight

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## ABSTRACT

Copolymerization of ethylene with propylene is carried out semi-continuously in toluene at atmospheric pressure and with various propylene/ethylene molar ratios. The polymerization temperature and cocatalyst/catalyst molar ratio were also varied in a wide range.  $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$  System was used as catalyst. The viscosity average molecular weights of copolymers obtained were determined by measuring the intrinsic viscosity  $[\eta]$  and application of the Mark-Houwink equation. The values of molecular weights were found to be dependent on operating conditions except on polymerization time in the range 5-30 min. Increasing the polymerization temperature, propylene/ethylene and cocatalyst/catalyst molar ratios caused a continuous decrease in molecular weight. An important reason for this effect was shown to be accelerated chain transfer reactions.

### Key Words:

EP copolymerization;  
semi-continuous reactor;  
bis-(cyclopentadienyl) zirconium  
dichloride;  
methylaluminoxane;  
viscosity average molecular  
weight;  
chain transfer reaction.

## INTRODUCTION

An important point of interest in developing homogeneous metallocene or as sometimes called "Kaminsky-Sinn catalysts" has been an academic motivation of introducing more simplified systems for mechanistic investigation of olefin

homo- and copolymerization. In this respect, these soluble catalysts have shed light on the proposed catalyst cycles by modelling some of the fundamental elementary steps such as olefin insertion or alkyl migration[1]. Kinetic consideration of

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olefin polymerization systems composed of these catalysts and application of various techniques have also led to determination of the nature of propagating species [2]. For these fascinating capabilities, the metallocene/methylaluminoxane systems are expected to play a decisive role in the future of olefin industry as they can produce new kinds of polyolefins with reasonably narrow molecular weight distribution for the existence of their single active centres and high activity as a result of higher concentration of active sites produced per unit catalyst [3-4].

However, a disappointing aspect in which homogeneous olefin polymerization by metallocene-based catalysts differs from heterogeneous Ziegler-Natta catalysis is that here low degrees of polymerization are achieved when propylene monomer is present. While ethylene is polymerized by MAO activated  $\text{Cp}_2\text{ZrCl}_2$  to give polymers with high molecular weights in the range of 100,000 to 1,000,000, the propylene copolymerization at room temperature produces polymers of rather low degrees of polymerization having molecular weights in the range of 200-1000 [5-6]. Such short polymer chains may not have any important industrial usefulness.

In the first part of this series, we studied the catalytic behaviour of the  $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$  system in copolymerization of ethylene with propylene for the semi-continuous procedure and examined the effects of process conditions on kinetics of the copolymerization [7]. In this part, we report the influence of some variables on average molecular weight of products obtained from the same copolymerization.

## EXPERIMENTAL

### Chemicals

The sources of polymerization materials, methods of purification and procedures for the preparation of dilute methylaluminoxane have been given previously [7]. Toluene was obtained from Aldrich and was refluxed and freshly distilled under argon from an Mg/K alloy. All polymerizations were carried out in toluene.

### Polymerization Technique

A 250 mL capacity jacketed glass-reactor fitted with an efficient water-cold condenser was used to perform the

polymerizations. The reactor was of the open-ended flanged type to facilitate the addition of catalyst, cocatalyst, and pure solvent through individual inlets. In this flow method, the monomers were supplied to the reactor semi-continuously via two restricting valves and a 3-way tap. In the reactor, part of each monomer was polymerized and the rest was discharged and measured by a wet flowmeter. More details of the polymerization system, its flowsheet and work-up of the product has been described elsewhere [7].

### Measurements of Viscosity

The viscosity of copolymers were determined in decaline (decahydronaphthalene) at about  $135^\circ\text{C} \pm 0.2$  by means of Ubbelohde suspended level dilution viscometer, [7]. A volume of 15 mL of decaline containing 0.1% w/v 2,6-di-*tert*-butyl-*p*-cresol antioxidant were placed in the viscometer reservoir and after the attainment of thermal equilibrium, the flow time,  $t_o$ , for pure decaline was measured. Subsequently, an accurately weight sample of copolymer (15 mg) was carefully dropped in the reservoir and dissolved completely by bubbling dry nitrogen and then the flowtime,  $t_p$ , was measured. Next to it, several 5 mL aliquots of decaline were added and each time after remixing, the new  $t_p$  was recorded. All experiments were performed in duplicated manner and timing for each experiment was recorded in triplicate.

The limiting viscosity numbers (LVN) were found by extrapolation of the data obtained from double plot of viscosity number and logarithmic viscosity number versus polymer solution concentration on a single graph as shown in Figure 1. The average of the two values was taken as the limiting viscosity number. Repeated experiments for the same sample and for

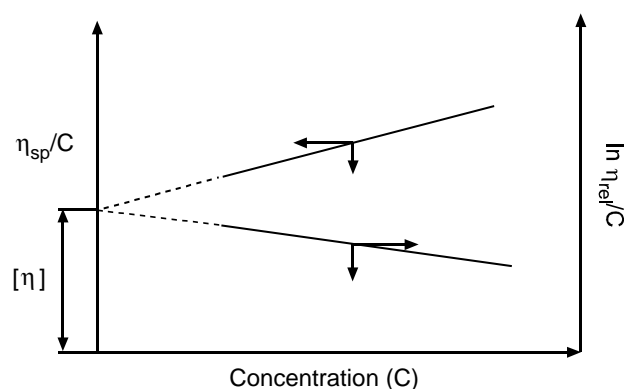


Figure 1. Plot of  $\eta_{sp}/C$  or  $\ln \eta_{rel}/C$  versus concentration.

samples prepared under the same polymerization conditions was found to lie within 3.6% each other.

Direct application of Mark-Houwink equation of the form  $[\eta] = 3.8 \times 10^{-4} \bar{M}_v^{0.74} \text{ dL.g}^{-1}$ , displayed the so-called viscosity average molecular weight,  $\bar{M}_v$  [8-13].

## RESULTS AND DISCUSSION

Viscosity measurements and application of Mark-Houwink equation is the simplest and most rapid method for determining the relative molecular weight of polymer [8]. So far there are several Mark-Houwink equations in the literature for EP copolymers differing in their “ $\alpha$ ” and “K” values [9-12]. We think that an important cause of the disagreements might be the type of copolymers of EP studied by different authors (statistic, graft, block and random). A widely employed equation was reported by Scholte et al. [11] and used by Pietikalnen and Seppala [12] for EP copolymers produced by the same catalyst system. This equation is that mentioned in experimental part and was used in this work. According to Maghami and Roberts, the K and  $\alpha$  parameters of this equation are almost constant over a wide range of propylene molar concentrations in the copolymer chains (20-45 mole%) and physical state of copolymers [13].

Depending on experimental polymerization conditions adopted in the present work, copolymers with a wide range of physical states from flowable and viscous to hard gels and solids were obtained indicating the serious effect of reaction conditions on life time of propagating species of  $\text{Cp}_2\text{ZrCl}_2$  in combination with

methylaluminoxane. By changing the conditions, copolymers with viscosity average molecular weights in the range 4,000 to 22,000  $\text{g.mol}^{-1}$  were resulted. All samples were also completely soluble in toluene between 25 and 60°C indicating that they were gel-free products.

The effect of main polymerization parameters on molecular weight was investigated by using the method outlined above in order to understand the magnitude and the type of termination processes which occur during the copolymerization since the molecular weight is in fact a consequence of competition between the chain growth and the chain termination reactions.

The variation of molecular weight with polymerization time is shown in Table 1. The effect is not significant, however, two opposing trends at moderate temperatures, e.g. 30°C, the  $\bar{M}_v$  values increased slightly with polymerization time a behaviour that has also been observed by Chien and Wang for ethylene polymerization using the same catalyst system [14]. Such increase of molecular weight with polymerization time was suggested by these authors to be due to a decrease in the concentration of the active catalytic complexes as the polymerization proceeds. However, this behaviour becomes reverse for samples prepared at higher temperatures i.e., 60°C, since a continuous drop in molecular weight was detected with increasing polymerization time probably due to increase in the number of polymer chains produced per unit catalyst per unit time as a result of either chains transfer acceleration or time-dependence active center formation (or both).

A more detailed examination of the influence of temperature on molecular weight was carried out. As

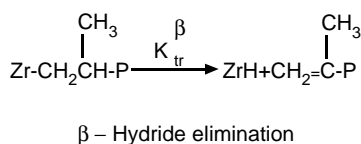
**Table 1.** Variation of  $[\eta]$  and  $\bar{M}_v$  with polymerization time.

Temperature (°C)	30		40		60	
Polymerization Time (min)	$[\eta]^*$	$\bar{M}_v^{**} \times 10^{-3}$	$[\eta]$	$\bar{M}_v \times 10^{-3}$	$[\eta]$	$\bar{M}_v \times 10^{-3}$
5	0.456	14.5	0.426	13.2	0.312	8.7
10	0.468	15.0	0.428	13.3	0.291	7.9
15	0.475	15.3	0.433	13.5	0.269	7.1
20	0.495	16.2	0.442	13.9	0.258	6.7
25	0.504	16.6	0.456	14.5	0.235	5.9
30	0.518	17.2	0.468	15.0	0.198	4.7

(\*): Number average viscosity ( $\text{dL.g}^{-1}$ ), (\*\*): viscosity average molecular weight ( $\bar{M}_v/\text{g mol}^{-1}$ ; polymerization conditions:  $\text{C}_3/\text{C}_2 = 50/50$ ,  $[\text{Zr}] = 5 \times 10^{-6}$  ( $\text{mol dm}^{-3}$ ),  $[\text{Al}]/[\text{Zr}] = 3000$ , solvent = toluene, and total pressure = 1 atm.

Table 2 shows, the polymerization temperature exerts a much stronger effect on the  $\bar{M}_v$  since it dramatically decreased by about 70% with increasing the temperature from 25 to 60°C. The Arrhenius plot of  $\bar{M}_v$  in Figure 2 confirms this dependency since its curve indicates a sharper slope at higher temperature regions. Therefore, it may be concluded that at low temperature the  $\bar{M}_v$  is only a function of polymerization time, all other conditions being kept constant.

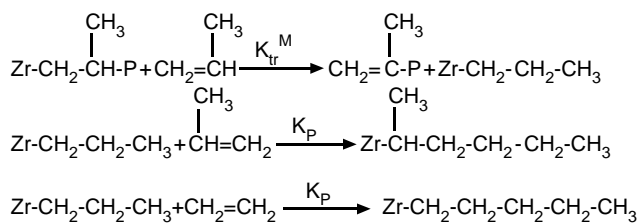
According to the related literature [15-16], there are two main transfer processes in absence of hydrogen addition. These are chain transfer to MAO with the rate constant  $K_{Al}^{tr}$  and the spontaneous process of  $\beta$ -hydride elimination with the rate constant  $K_{Al}^{\beta}$ . The latter has been shown to be of more important for  $Cp_2ZrCl_2/MAO$  catalyst [16] (Scheme I).



**Scheme I**

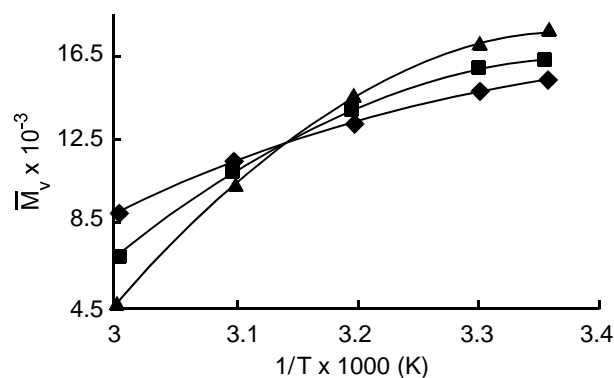
The relatively lower molecular weights obtained at higher temperatures must, therefore, be due to a decrease in the rate of olefin insertion or an increase in the rate of chain terminating transfer reactions and the average degree of polymerization is then determined by the ratio of chain propagation and chain termination.

Tsutsui et al. [17] have investigated the microstructures of EP copolymers prepared in the presence of  $Cp_2ZrCl_2/MAO$  by  $^{13}C$  NMR spectroscopy. According to their report, the chain transfer reaction is most probably caused by propylene monomer when the propagating chain end is propylene unit, viz (Scheme II):



**Scheme II**

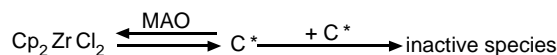
Therefore, one can conclude that chain transfer reaction is most facilitated when the last added monomer into propagating chain is propylene.



(♦)  $t = 10$  min; (■)  $t = 20$  min; (▲)  $t = 30$  min.

**Figure 2.** Arrhenius plot of  $\bar{M}_v$  versus  $(1/T)$ .

$[MAO]/[Zr]$  ratio is another influencing parameter on molecular weight as shown in Table 3. The molecular weight decreased slightly and almost linearly by keeping the MAO concentration constant and increasing the  $Cp_2ZrCl_2$  concentration. Molecular weights are higher substantially at low zirconium concentrations. This might be due to dilution effects favoring the dissociated or olefin-separated ion pairs  $C^*$  relative to their associated precursors  $C$ , and hence increasing the rate of chain propagation over that of chain termination. Kaminsky and co-workers advocated that a bimolecular reaction of the active complex with a second zirconocene species terminates growth of the polymer chain in a manner possibly related to the second-order deactivation process [18-19] (Scheme III).



**Scheme III**

This behaviour may lead to the conclusion that for chain transfer reaction to occur, a bimetallic mechanism is necessary if one accepts that nearly all the Zr complexes are catalytically active. Further clarification of this behaviour can be expected from future studies on MAO-free metallocene polymerization catalysts.

In another series of polymerization experiments the concentration of MAO was changed at constant  $[Cp_2ZrCl_2]$ . The data collected in Table 4 indicate that a more intense effect arises from  $[MAO]$  than from  $[Cp_2ZrCl_2]$  because a sharper decrease in molecular weight was detected by increasing  $[MAO]/[Zr]$  from  $1 \times 10^3$  to  $3 \times 10^3$ . The decline in  $\bar{M}_v$  became then slight

**Table 2.** Effect of polymerization temperature on  $\bar{M}_v$  at different mean residence times.

Time (min)	10		20		30	
Temperature (°C)	$[\eta]^*$	$\bar{M}_v^{**} \times 10^{-3}$	$[\eta]$	$\bar{M}_v \times 10^{-3}$	$[\eta]$	$\bar{M}_v \times 10^{-3}$
25	0.482	15.6	0.500	16.4	0.533	17.9
30	0.468	15.0	0.495	16.2	0.518	17.2
40	0.428	15.3	0.442	13.9	0.461	14.7
50	0.382	11.4	0.375	11.1	0.354	10.3
60	0.365	8.9	0.342	6.7	0.198	4.7

Polymerization conditions are shown in Table 1.

**Table 3.** Variation of  $[\eta]$  and  $\bar{M}_v$  with  $[\text{Zr}]$ .

$[\text{Zr}]/\text{mol dm}^{-3}$	$2 \times 10^{-6}$		$5 \times 10^{-6}$		$6.7 \times 10^{-6}$		$1.3 \times 10^{-6}$	
Mean residence time/min	$[\eta]$	$10^{-3} \bar{M}_v$	$[\eta]$	$10^{-3} \bar{M}_v$	$[\eta]$	$10^{-3} \bar{M}_v$	$[\eta]$	$10^{-3} \bar{M}_v$
10	0.450	14.2	0.428	13.3	0.423	13.1	0.382	11.4
20	0.433	14.7	0.433	13.9	0.411	12.6	0.404	12.3
30	0.480	15.5	0.461	14.7	0.499	14.2	0.423	13.1

Polymerization conditions:  $C_3/C_2 = 50/50$ ,  $[\text{A}] = 1.5 \times 10^{-2} \text{ mol dm}^{-3}$ , Temperature = 40°C, solvent = toluene, pressure = 1 atm.

**Table 4.** Effect of MAO concentration on  $\bar{M}_v$ .

$[\text{Al}]/[\text{Zr}]$ Ratio (mol/mol)	$1 \times 10^3$	$2 \times 10^3$	$3 \times 10^3$	$4 \times 10^3$	$5 \times 10^3$
$[\eta]/\text{dL g}^{-1}$	0.613	0.477	0.402	0.336	0.275
$\bar{M}_v \times 10^{-3}/\text{g.mol}^{-1}$	21.6	15.4	12.2	9.6	7.3

Polymerization conditions:  $C_3/C_2 = 60/40$ , Temperature = 40°C,  $t = 20$  min,  $[\text{Zr}] = 5 \times 10^{-6} \text{ mol dm}^{-3}$ , solvent = toluene, total pressure = 1 atm.

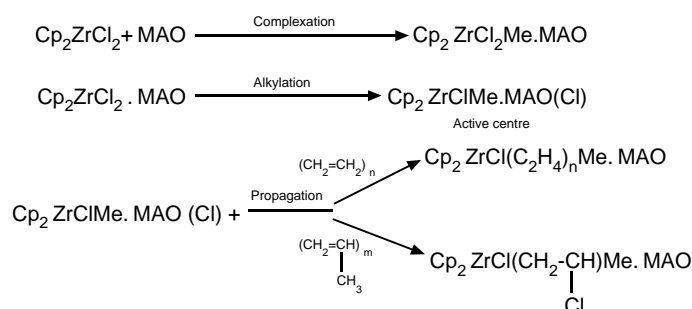
by further increase of this ratio.

This observation leads to assume two different roles for MAO in the present polymerization system. The first is to alkylate the zirconocene catalyst after initial complex formation as a result of which active species are formed and propagate (Scheme IV).

The second role of MAO is to function as chain

transfer agent, viz, (Scheme V).

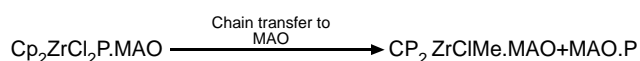
Therefore, this transfer to MAO should be competitive with chain transfer with propylene and by  $\beta$ -H elimination. However, the higher  $\bar{M}_v$  produced at low concentrations of MAO may be accounted for a slower transfer since the majority of these species are involved either in alkylated  $\text{Cp}_2\text{ZrClMe.MAO}$  form or in propa-

**Scheme IV**

**Table 5.** Effect of propylene mol % on  $\bar{M}_v$  of copolymer.

Temperature (°C)	40		60	
C <sub>3</sub> mol % in gas mixture	[ $\eta$ ]	$\bar{M}_v \times 10^{-3}$	[ $\eta$ ]	$\bar{M}_v \times 10^{-3}$
50	0.442	13.9	0.342	6.7
60	0.402	12.2	0.208	5
70	0.349	10.1	0.173	3.9
80	0.241	6.1	0.342	3.2

Polymerization conditions:  $[\text{Zr}] = 5 \times 10^{-6} \text{ mol dm}^{-3}$ ,  $t = 20 \text{ min}$ ;  $[\text{Al}]/[\text{Zr}] = 3000$ , solvent = toluene, total pressure = 1 atm.



### Scheme V

gating [20] sites of the form  $\text{Cp}_2\text{ZrClIP.MAO}$ .

Finally, the  $\bar{M}_v$  of a series of samples produced with differing propylene/ethylene molar ratios at other constant conditions was studied. The results are listed in Table 5. It is clear here again that propylene acts as a chain transfer agent, because by increasing its molar fraction in the gas feed, the molecular weight decreases very considerably. In addition the most likely  $\beta$ -H chain elimination has been reported to have higher rate constant for propylene compared to ethylene due to labile  $\beta$ -hydrogen being associated with the former [21-22].

## CONCLUSION

In conclusion, we have found that non-support,  $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$  catalyst system produces almost low molecular weight EP copolymers. However, it is possible to rise the molecular weight of product by carefully adjusting the polymerization conditions such as propylene feed molar fraction, polymerization temperature, MAO concentration, etc. Both propylene and MAO act as chain transfer agents and as the polymerization temperature increases, these effects become more profound.

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